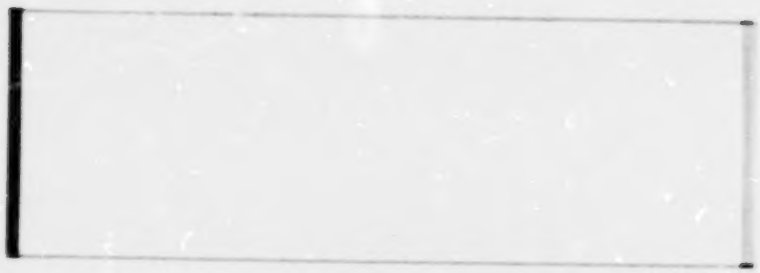

CHEMEX LABS LTD.

RADIOCHEMICAL DETERMINATION OF CCRMP REFERENCE MATERIALS FOR CERTIFICATION PURPOSES: LEAD 210 ACTIVITY MEASUREMENTS.

RADIOCHEMICAL DETERMINATION OF CCRMP REFERENCE MATERIALS FOR CERTIFICATION PURPOSES: LEAD 210 ACTIVITY MEASUREMENTS.

FINAL REPORT

BY

CHEMEX LABS LTD.

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Canada

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1. Introduction

Chemex Labs has determined the lead-210 activity in four reference materials DL-1a, DH-1a, BL-4 and BL-5. Measurements have been performed in quadruplicate by both radiochemical procedures and by gamma spectroscopy.

2. Personnel

Dr. Michael LeGeyt has been contract manager for this proposal and in this capacity has prepared the final report and coordinated the project.

Dr. Henk Blok has been responsible for the gamma spectroscopy measurements and Mrs. Eva Savoy has performed the radiochemical separations and beta counting.

3. Methodology

3.1. Overview

Chemex has used a Canberra Model 2200 Alpha, Beta Analyzer to determine lead-210 activity by beta counting following a radiochemical separation. This instrument contains an external proportional counter with an ultra-thin detector window. The counter is completely surrounded by four inches of virgin lead and utilizes ultrahigh purity P-10 counting gas (90% argon - 10% methane).

To measure lead-210 activity, Chemex used a radiochemical analytical procedure in which lead-210 is determined indirectly by measurement of its high-energy beta emitting daughter bismuth-210. A general description of the procedure is as follows:

A mixed carrier solution containing stable lead and bismuth is added to a 1.0 gm sample which is then digested with a mixture of nitric, hydrofluoric and perchloric acids until only a small volume of fuming perchloric acid remains. If undigested material is still present, the digestion is repeated to yield a clear digest when taken up in 2M HCl. Lead and bismuth are extracted into chloroform with diethyldithiocarbamate and then back extracted into aqueous solution. The bismuth concentration of this aqueous solution is then determined by atomic absorption spectrophotometry to determine the recovery of bismuth (typically 95-100%) through the extraction procedure. The bismuth present is subsequently precipitated and purified as the oxychloride. The precipitate is collected on a 0.45u membrane filter in a ring and disc filter assembly, air-dried briefly and then covered with aluminum foil. The aluminum foil serves to screen out week beta emission from lead-210 as well as alpha emission from polonium-210 which is carried through the procedure.

The beta activity of the precipitated bismuth oxychloride is then counted for 100 mins. and compared to the activity of standard lead-210 and bismuth-210 solutions carried through the same procedure. Certified reference materials and lead-210 solutions of standard activity are also analyzed with each batch. Ref: CANMET Report No. 78-22, G. Smithson Ed. (1979)pp. 19-22.

Gamma spectroscopy measurements were performed with a high efficiency (17%) lithium-drifted germanium detector connected to a 16,000 channel Ortec Model 7044 multichannel analyzer controlled by a PDP 11/34 computer with 256K bytes of memory. The detector was shielded by a lead cave of 15x15x20 inches. The walls of the cave are four inches thick and are lined with 0.02 inches of cadmium and 0.06 inches of copper to absorb x-rays generated in the lead by gamma rays emitted by the sample.

Using the gamma spectroscopy system, lead-210 was determined directly by measurement of its 46.5 KeV gamma ray. Sample size used for this measurement was typically 30-70 gms. Samples were hermetically sealed for sixty days to permit ingrowth of radon-222 and the establishment of equilibrium with lead-210. An ingrowth period of this duration permits 99.998% equilibrium between radon-222 and lead-210 and thus does not compromise the validity of the lead-210 measurement.

Counting periods for gamma spectroscopy analyses ranged from 10,000 Secs. to 40,000 Secs. depending on sample activity.

3.2. Radiochemical Calibration

For the radiochemical analyses, calibration has been carried out using a lead-210/bismuth-210 standard reference solution of Amersham Corporation, Catalogue No. RBZ.44. Calibration consisted of 27 separate determinations in the range of 0-2 Bq. The standard curve was derived by linear regression analysis of the function of the observed net beta counts of bismuth-210 with respect to various aliquots of bismuth-210.

The equation of the standard curve derived was as follows:

$$y=67.4x + 29$$

where y represents beta counts of bismuth-210 and x represents lead-210 activity in picoCuries. The standard deviation of the slope was calculated to be ±0.92 and the standard deviation of the intercept was calculated to be ±25.4. The coefficient of correlation of the standard curve was 0.9977 and the reproducibility was ±15% (n=5) at the 0.15 Bq level and ±3% (n=5) at the 2 Bq level.

The calculation of the basic curve by linear regression is sufficiently straight forward that this calculation has not been included. The formulae used for the calculation of the uncertainties of the slope and intercept as well as example calculations are shown in Appendix I.

3.3 Radiochemical Analyses

Samples taken for analysis were at least 1 gm. in order to minimize subsampling errors. However because of the elevated activity of the samples at this mass it was necessary to take an aliquot of the digest solution for subsequent analysis. The general procedure followed has been outlined in Sec. 3.1.

Following precipitation and collection of bismuth oxychloride, the precipitate was stored for 24 hours prior to beta counting. Counting times for all standards, samples and blanks were 100 minutes.

A sample calculation of the activity of DL-1a in one such analysis, along with its associated uncertainty is shown in Appendix 2. For the purposes of the uncertainty calculation, the uncertainty in each weighing is estimated to be ±0.0001 g and the uncertainty in pipetting is that listed by the manufacturers, ±0.3% for 1 ml Eppendorf pipettes and ±0.03 mls for 25 ml glass pipettes. Since counting times were constant for all standards, samples and blanks, and since the uncertainty in the time measurement is considered insignificant, time has been factored out of the uncertainty calculations.

Table 1 lists the radiochemical analytical results and their uncertainties at the 95% confidence level of the four samples analyzed as part of this contract.

TABLE 1

Lead-210 Activity of CCRMP Reference Materials

(Radiochemical Analyses)

Sample	Mass of Sample Digested (g)	Mass of Analyzed Subsample (g)	Pb-210 Activity (Bq/g)	Uncertainty (95%) (Bq/g)
DL-1a	2.0635	0.5159	1.38	0.12
DL-1a	2.1063	0.5267	1.38	0.12
DL-1a	2.1216	0.5304	1.47	0.12
DL-1a	2.0762	0.5191	1.44	0.12
DH-1a	1.0036	0.05018	33.3	1.9
DH-1a	1.0040	0.05020	33.3	1.9
DH-1a	1.0050	0.05025	33.9	1.9
DH-1a	1.0060	0.05030	33.6	1.9
BL-4a	1.0858	0.10858	15.0	0.8
BL-4a	1.0693	0.10693	14.8	0.8
BL-4a	1.0014	0.10014	14.8	0.8
BL-4a	1.0949	0.10949	15.4	0.8
BL-5	1.0085	0.0020170	875	49
BL-5	1.0098	0.0020196	902	49
BL-5	1.0002	0.0020004	869	49
BL-5	1.0549	0.0021098	912	49

4.1 Gamma spectroscopy measurement of lead-210 content

Two different size sample containers were used for the counting of the 46.5 KeV gamma ray. Both containers were cylindrical 2 in. diameter ultra thin plastic cups. One size is one inch high, while the other one was one-half inch high. Nominal volumes were 50 and 25 c.c. respectively.

Samples were packed into these containers, sealed and allowed to establish equilibrium for sixty days. Standards were prepared from a lead-210 bismuth-210 standard reference solution of Amersham Corporation Catalogue No. RBZ.44.

Counting time, net peak area, weight of the sample used, sorption correction factor and calculated activity are shown in table 2.

4.2 Sorption correction

The most important correction factor used in the calculations is the sorption correction factor. The number of photons sorbed is dependent on the photon cross-section, the average path length, the weight and the volume of the source. The photon cross-section is proportional to the atomic number (Z) of the matrix constituents, the molecular weight fraction of the matrix and the energy of the photon.

The effect of sorption can be expressed as:

$$Ac = Ao \cdot \frac{\mu x}{1 - e^{-\mu x}}$$

where
Ac is the sorption corrected activity
Ao is the observed activity (net peak area)
μ is the photon cross-section in grams^{-1}

$$\left[\frac{cm^2}{g} \text{(photon cross-section)} . \text{cm (path length)} \cdot \frac{1}{cm^3} \text{ (volume)} \right]$$

x is the weight of the sample

In order to calculate μx, the composition of the matrix has to be known. Composition values were taken from the CANMET data sheets for each of the samples, while the photon cross-section values were obtained by interpolation of the data in "Photon Cross-Sections from 1 KeV to 100 MeV for elements Z=1 to Z=100", E. Storm and H. I. Israel, Nuclear Data Tables, Volume F, Number 6, (1970).

TABLE 2

Lead-210 Activity of CCRMP Reference Material

Gamma Spectroscopy Analyses

Sample	Weight Used (g)	Counting Time (sec)	Net Peak Area	Sorption Correction Factor	Pb-210 Activity Bq/g	Uncertainty Bq/g
DL-1a	64.598	40,000	9428	1.369	1.39	.18
DL-1a	63.346	40,000	9210	1.342	1.36	.17
DL-1a	63.932	40,000	9167	1.355	1.35	.17
DL-1a	64.173	40,000	9099	1.360	1.34	.18
DH-1a	65.599	10,000	42307	1.676	30.1	3.19
DH-1a	64.553	10,000	40540	1.650	28.8	3.7
DH-1a	60.500	10,000	39563	1.546	28.1	3.7
DH-1a	63.815	10,000	43633	1.631	31.0	3.9
BL-4a	32.576	10,000	20010	1.339	15.0	2.2
BL-4a	31.606	10,000	20005	1.299	15.0	2.2
BL-4a	34.380	10,000	20851	1.412	15.7	2.2
BL-4a	32.924	10,000	20203	1.353	15.2	2.2
BL-5	31.123	10,000	553663	2.837	923.	130
BL-5	32.601	10,000	549139	2.972	915.	130
BL-5	34.489	10,000	568775	3.144	948.	130
BL-5	33.973	10,000	557412	3.097	929.	130

Table 3: μx values obtained for each of the sample types, assuming an average weight of 63 gm and 32 g for the large and small containers repectively.

Sample	Container	μx	Sorption factor
DH1a	large	1.042	1.610
DL1a	large	0.608	1.335
BL4a	small	0.576	1.315
BLA	small	2.726	2.917
Water	large	0.120	1.061
Water	small	0.087	1.044

4.3 Uncertainty Calculation

There are three main components of the uncertainty of the calculated activity. There are:

a) uncertainty due to counting statistics, peak stripping counting geometry and sample weights
b) uncertainty in the calculation of the activity of the standards used
c) uncertainty in the calculation of the sorption correction factors.

We can best demonstrate this by following through an entire activity calculation.

Sample DL1a

weight of sample	64.598 g ± 0.003 g
gross peak area	28909 counts ± 170
background	19481 counts ± 480

(Background uncertainty is ±30 counts/channel x 16 channels)
net peak area per grams of sample is 145.9 ± 4.5

Similarly, the uncertainty in the standard due to counting statistics of peak stripping can be calculated and gives 143.8 ± 3.7 counts per Bq. The largest uncertainty is in the calculation of the sorption corrections factor.

Photon cross-sections are only good to ±5% at best, while the bulk composition of the sample is assumed to also be known to no better than 5%. As many as 18 components make up the overall photon cross-section, but only 3 or 4 of these are significant contributions to the total.

For DL1a the main contributors to the photon cross-section are O, Al, Si, S, K, Ca and Fe. The uncertainty in the cross-section calculations is evaluated from:
[oxygen] (.5257±5%)x(.0579±5%)+[Aluminum](.0525±5%)x((.268±5%) +[Silica] (etc.)
and works out to a total uncertainty of 12%

The overall uncertainty is $\left[12^2+2.5^2+3.1^2\right]^{1/2} = 12.6\%$

The main point that should be stressed is that the activity value calculated is only as good as one can calculate a sorption correction value. A small percentage of heavy elements in the sample will significantly affect the final results. The indicated uncertainties principally reflect the uncertainty in the sorption correction factor.

Appendix I

Calibration Uncertainty Calculation

1. Variance of Y with respect to X.

The following formula has been used to calculate the variance (V) of Y, the observed net beta counts of bismuth-210, versus X, the added picoCuries of bismuth-210:

$$(n-2)V = \Sigma(Yo-Yc)^2$$

where (n-2) degrees of freedom are used because the data have been used to estimate both the slope and the intercept and (Yo-Yc) represents the deviations of the experimental readings from the line that best fits the data.

$$\therefore 25V = 170778$$

$$\text{and } V\ (Y/X) = 6831.12$$

$$\text{and } s\ (Y/X) = 82.65$$

2. Standard Deviation of the slope, s(m).

The following formula was used to calculate the standard deviation of the slope:

$$s(m) = s(Y/X)/[\Sigma(X-\bar{X})^2]^{1/2}$$

where $(X-\bar{X})$ represents the difference between individual and mean values of X.

$$\therefore s(m) = 82.65/(8140.33)$$

$$= 0.92$$

$$\therefore s^2(m) = 0.84$$

3. Standard Deviation of the Intercept, s(b)

The following formula was used to calculate the standard deviation of the intercept s(b):

$$s(b) = s(Y/X)\left[\frac{\Sigma X^2}{n\Sigma(X-\bar{X})^2}\right]^{1/2}$$

$$= 82.65\left[\frac{20832.66}{27 \times 8140.33}\right]^{1/2}$$

$$= 25.4$$

$$\therefore s^2(b) = 645$$

Appendix II

Sample Calculation

Sample DL-1a

1. wt. of sample = 2.0635 ± 0.0002 g (0.0001 g uncertainty/weighing)
Sample was digested, transferred to a 100.00 ± 0.08 ml flask, and 25.00 ± 0.03 mls withdrawn for analysis.

$$\text{actual weight in analyzed aliquot} = 2.0635 \pm 0.0002 \text{ g} \times \frac{25.00 \pm 0.03}{100.00 \pm 0.08}$$

$$= 2.0635 \pm 0.1 \text{ ppt} \times \frac{25.00 \pm 1.2 \text{ ppt}}{100.00 \pm 0.8 \text{ ppt}}$$

$$= 0.5159 \pm (0.1^2 + 1.2^2 + 0.8^2)^{1/2}$$

$$= 0.5159 \pm 0.0007 \text{ g}$$

2. Counting

Counting times for all standards, samples and blanks were 100 mins and since the relative error in the timer is considered insignificant, the time has been factored out of all the uncertainty calculations.

Detector background = 140 counts ± $140^{1/2}$ = 140 ± 12
Sample + background = 1206 counts ± $1206^{1/2}$ = 1206 ± 35
net counts = (1206 ± 35) − (140 ± 12)
= 1066 ± $(35^2 + 12^2)^{1/2}$
= 1066 ± 37

The sample was counted 1.187 days following precipitation of BiOCl and the recovery of 1 mg of bismuth was determined to be 95 ± 1%. The uncertainty of +1% represents 1 division on an AA readout. To correct for the decay of Bi-210 and the yield, the following expression is used:

$$\text{Corrected counts} = \frac{\text{Net counts}}{E.w.E^{-\lambda t}}$$

where E represents the yield, the decay constant, w the weight of bismuth added and t the elapsed time since precipitation.

$$\text{Therefore, corrected counts} = \frac{1066 \pm 37}{(0.95 \pm 0.01)\ (1.000 \pm 0.003)\ e^{-0./1386 \times 1.187}}$$

$$= \frac{1066 \pm 34.7 \text{ ppt}}{(0.95 \pm 10.5 \text{ ppt})\ (0.8483)(1 \pm 3 \text{ ppt})}$$

$$= 1323 \pm (34.7^2 + 10.5^2 + 3^2)^{1/2}$$

$$= 1323 \pm 36 \text{ ppt}$$

$$= 1323 \pm 48 \text{ counts}$$

3. Calculation from Standard Curve

The equation of the standard curve is:

$$y = (67.4 \pm 0.92)x + (29 \pm 25.4)$$

where y represents beta counts of Bi-210 corrected for yield and ingrowth and x is the activity of Bi-210 in picoCuries

$$1323 \pm 48 = (67.4 \pm 0.92)x + (29 \pm 25.4)$$
$$1294 \pm (48^2 + 25.4^2)^{1/2} = (67.4 \pm 0.92)x$$
$$1294 \pm 54 = (67.4 \pm 0.92)x$$

$$x = \frac{1294 \pm 54}{67.4 \pm 0.92} = \frac{1294 \pm 41.7 \text{ ppt}}{67.4 \pm 13.6 \text{ ppt}} = 19.2 \text{ pCi} \pm (41.7^2 + 13.6^2)^{1/2}$$

$$= 19.2 \text{ pCi} \pm 43.9 \text{ ppt}$$

$$= 19.2 \pm 0.8 \text{ pCi}$$

4. Correction for weight:

This activity is associated with 0.5159 ± 0.0007 gms of sample.

the sample activity is $\frac{19.2 \pm 0.8}{0.5159 \pm 0.0007} = 37.2 \pm 1.6$ pCi/gm at the 67% confidence level

At the 95% confidence level, sample activity is

$37.2 \pm (1.96 \times 1.6)$ pCi/gm
or 37.2 ± 3.1 pCi/gm
or 1.38 ± 0.12 Bq/gm

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